

# Measurement of Translational Diffusion Constant using Noon State

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## Abstract

A method for measuring translational diffusion constant in liquids via NOON state is described using a quantum circuit and is experimentally demonstrated using a model system. When compared with the standard single quantum method, the NOON state method requires shorter diffusion delays and weaker gradients. These improvements depend on the size of the NOON state. Due to the high sensitivity of the NOON state for the changes in the local magnetic fields, this method enables studying slow diffusion and studying diffusion with limited strengths of pulsed-field-gradients.

*Key words:* NOON state, diffusion, multiple-quantum coherence, pulse-field-gradient

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## 1 Introduction

Driven by the internal thermal energy, the atoms or molecules of a bulk matter exhibit random translational motion, which is termed as translational diffusion [1,2]. Diffusion explains the net flux of particles moving from a region of higher concentration to the lower concentration, although diffusion process exists even when there is no macroscopic concentration gradient. Diffusion is a fundamental transport mechanism in liquids and gasses and therefore measurement of diffusion constant is important for understanding many physical, chemical, and biochemical processes [3,4,5,6]. The diffusion constant ( $D$ ) is described as the amount of a particular substance that diffuses across a unit area in unit time under the influence of a unit concentration gradient [1]. According

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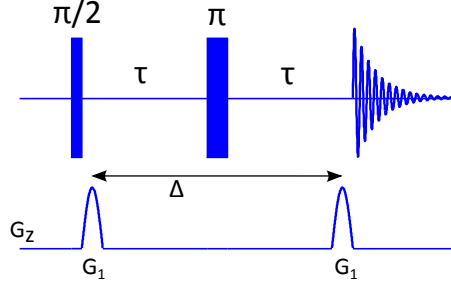


Fig. 1. Hahn-echo pulse sequence with two equal PFGs for the measurement of diffusion constant.

to the Stokes-Einstein theory, for a fluid with viscosity  $\eta$  at a temperature  $T$ , the diffusion constant is given by

$$D = \frac{kT}{6\pi\eta r_s}, \quad (1)$$

where  $k$  is the Boltzman constant and  $r_s$  is the Stokes radius of the diffusing particle [7,8]. The denominator in the above expression is termed as the friction coefficient.

Diffusion constant of a liquid can be measured by NMR either with the help of relaxation studies or more conveniently using pulsed-field-gradients (PFGs) [9]. Fig. 1 shows a standard pulse sequence based on the Hahn-echo method for measuring diffusion constant [10,11]. In this method, maximum amplitude of Hahn-echo can be obtained by a refocussing  $\pi$  pulse placed between two PFGs if the molecules do not change their place during the period  $\Delta$ . Diffusion renders the molecules to change their place and therefore for a fixed duration  $\Delta$ , the echo amplitude decreases with the strength of the PFGs. Such PFG methods are widely used for the measurement of diffusion constants and already numerous improved sequences are available [12,13,14]. For example, replacing Hahn-echo by stimulated-echo sequence reduces the decay due to transverse relaxation and results in enhanced echo amplitudes [15,16]. Application of long-lived singlet states allows one to study slow diffusion requiring long intervals ( $\Delta$ ) between the PFGs [17]. Fast single-scan measurement of diffusion has also been demonstrated by realizing z-coordinate dependent PFG strengths using frequency swept refocusing pulses [18].

In this letter we describe another approach inspired by quantum information theory to speed-up the measurement of diffusion constant. We propose to prepare the diffusing spin system into a NOON state. Although this method has similarities with the multiple-quantum method for studying diffusion [19,20,21], the current method differs in actual implementation and its scope. We briefly outline the theory in section 3 and we describe the experimental demonstration in section 4.

## 2 Diffusion constant by NOON state

### 2.1 NOON state

We shall follow the notations of quantum information theory where  $\pm 1/2$  states of a spin  $1/2$  nucleus is represented by basis kets  $|0\rangle$  and  $|1\rangle$  of a quantum bit or a ‘qubit’. The NOON state of an  $N$ -qubit system is a superposition of all the  $N$  qubits being in state 0 with all those in state 1:

$$\begin{aligned} |N00N\rangle &= (|N, 0\rangle + |0, N\rangle)/\sqrt{2} \\ &= (|00\cdots 0\rangle + |11\cdots 1\rangle)/\sqrt{2} \end{aligned} \quad (2)$$

[22]. Recently several applications of NOON states have been discovered [23,24,25]. It has also been used for sensing weak magnetic fields [26].

The circuit for the preparation of NOON state, shown in the first part of Fig. 2, consists of a Hadamard gate (H) and a CNOT gate. This circuit acts on a quantum register with a single ‘control’ qubit and a set of  $(N - 1)$  ‘target’ qubits initialized in  $|00\cdots 0\rangle$  pure state

$$\begin{aligned} |00\cdots 0\rangle &\xrightarrow{H_{\text{control}}} \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)|00\cdots 0\rangle \\ &\xrightarrow{\text{CNOT}} \frac{1}{\sqrt{2}}(|00\cdots 0\rangle + |11\cdots 1\rangle) = |N00N\rangle. \end{aligned} \quad (3)$$

Preparing a pure NOON state is out of bounds from a highly mixed thermal equilibrium state that is available in liquid state NMR systems at ordinary temperatures. However, it is rather easy to prepare a pseudopure NOON state which is of the form

$$\rho_{N00N} = \frac{1 - \epsilon}{2^N} \mathbb{1} + \epsilon |N00N\rangle\langle N00N|, \quad (4)$$

where the scalar quantity  $\epsilon$  is a measure of purity, which is of the order of  $10^{-5}$  in typical NMR setups [27]. The identity part does not evolve under unitary dynamics neither does it give rise to NMR signals. Therefore we ignore this part as a background and continue using ket notation  $|N00N\rangle$  for simplicity.

The CNOT implementation is particularly easier with a heteronuclear spin system of type  $AM_{N-1}$ , wherein each M spin of the  $N - 1$  magnetically equivalent spins, is having an indirect spin-spin interaction with the common heteronuclear spin A with a coupling constant of, say  $J$  Hz. We shall use the single

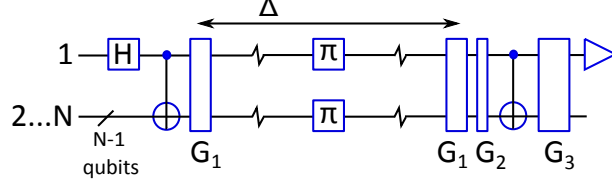


Fig. 2. Circuit for the measurement of diffusion constant using NOON state. NOON state is initialized using a Hadamard gate (H) and a CNOT ( $\oplus$ ) gate. The diffusion of particles is monitored using two identical PFGs of strength  $G_1$  placed on either side of  $\pi$  pulses. The second CNOT converts the evolved NOON state into an observable single quantum coherence of the 1st qubit. The signal of the first qubit is measured after the PFGs  $G_2$  and  $G_3$  select the coherence transferred from the NOON state.

heteronucleus as the ‘control’ qubit and the rest as the ‘target’. Such a system allows parallel implementation of CNOT gate (upto a global phase) using the sequence

$$U_{\text{CNOT}} = Y_A^2 \bar{Y}_M U_J Y_{A,M}^2 U_J \bar{Y}_A \bar{X}_A Y_A \bar{Y}_M \bar{X}_M \quad (5)$$

[28,29]. Here  $X = e^{-i(\pi/2)I_x}$  and  $\bar{X} = e^{+i(\pi/2)I_x}$  are rotations on the spins indicated by their subscripts ( $I$  is the spin operator and  $Y, \bar{Y}$  are defined similarly). Under  $U_J = e^{-i(\pi/2)JI_z^A \sum_M I_z^M}$  all the target qubits simultaneously undergo J-evolution with the control and is realized simply by a  $1/(4J)$  delay. In our experiments we have replaced the Hadamard gate on A with a pseudo-Hadamard gate which can be implemented by a single  $Y_A$  pulse. The rest of the circuit in Fig. 2 is described in the following.

## 2.2 Phase encoding and diffusion measurement

Consider first the simple Hahn-echo sequence for measuring the diffusion constant as illustrated in Fig. 1. For simplicity, we ignore decoherence and other experimental errors in the following analysis. The first gradient encodes the longitudinal distribution of the sample such that a spin in position  $z$  gets a phase  $\phi(z) = \gamma z G_z \delta$ , where  $\gamma$  is the gyromagnetic ratio of the spin and  $\delta$  is the effective duration (duration  $\times$  shape-factor) of the gradient  $G_z$ . Under this gradient the pseudopure coherence  $|0\rangle + |1\rangle$  (ignoring the background) evolves to  $|0\rangle + e^{i\phi}|1\rangle$ . After the central  $\pi$  pulse flips the basis states the second gradient encodes another identical phase so that the resulting state becomes  $e^{i\phi}|1\rangle + e^{i\phi}|0\rangle \equiv |0\rangle + |1\rangle$ , up to a global phase. Thus if the spin does not change the position there is no change in the relative phase. However if, during the period  $\Delta$ , the spin changes the position by an effective amount  $dz$ , the state after the second gradient will be  $|0\rangle + e^{id\phi}|1\rangle$ , where the relative phase is  $d\phi = \gamma dz G_z \delta$ .

Due to the random molecular motion of a large number of spins each of which acquiring a different relative phase, the average Hahn-echo does not acquire a net phase but diminishes in amplitude. Theoretically, the decay of the Hahn-echo signal  $S$  can be given as,

$$S(G_z) = S_0 \exp \left\{ -\gamma^2 G_z^2 \delta^2 D (\Delta - \delta/3) \right\}, \quad (6)$$

where  $D$  is the diffusion constant,  $S_0 = S(0)$  is the normalization factor, and  $\Delta - \delta/3$  is the correction to  $\Delta$  due to the finite durations  $\delta$  of the PFGs [12].

Similar analysis can now be carried out for the NOON state using the circuit shown in Fig. 2. Under the  $G_1 - \pi - G_1$  sequence, a spin system in NOON state diffusing through a distance  $dz$  acquires a net relative phase and becomes  $(|00 \cdots 0\rangle + e^{id\phi}|11 \cdots 1\rangle)/\sqrt{2}$ . The relative phase acquired is  $d\phi = \gamma_{\text{eff}} dz G_z \delta$ , where  $\gamma_{\text{eff}} = \{1 + (N-1)\gamma_M/\gamma_A\}\gamma_A = l\gamma_A$ . The factor  $l$  is also known as ‘loopsidedness’ of the NOON state. Larger the value of  $l$ , more sensitive is the NOON state for the phase encoding. Since NOON state is a multiple quantum coherence it is necessary to convert it back to single quantum coherence before detection. This conversion can efficiently be carried out using a second CNOT gate:

$$\frac{1}{\sqrt{2}}(|00 \cdots 0\rangle + e^{id\phi}|11 \cdots 1\rangle) \xrightarrow{\text{CNOT}} \frac{1}{\sqrt{2}}(|0\rangle + e^{id\phi}|1\rangle)|00 \cdots 0\rangle. \quad (7)$$

Thus the phase encoding due to the diffusion, i.e.,  $d\phi$  has been transferred to one transition of the control spin. However as explained before, for a large number of molecules undergoing diffusion, the above phase encoding results in the attenuation of the control transition. Instead of starting with an initial pseudopure state, it is rather convenient to start with a thermal equilibrium state and use two PFGs  $G_2$  and  $G_3$  to select out the desired coherence pathway that is passing through the NOON state. The ratio of these two PFGs are adjusted depending on the relative gyromagnetic ratio:  $G_3 = G_2((N-1)\gamma_M/\gamma_A + 1)$ .

In the case of large loopsidedness  $l$ , the NOON state helps us to study diffusion with weaker PFGs and smaller durations ( $\Delta$ ) between them. An experimental demonstration of this method for a model system is described in the following section.

### 3 Experiment

The sample consisted of 100  $\mu\text{l}$  of trimethylphosphite (see inset of Fig. 3) dissolved in 500  $\mu\text{l}$  of dimethyl sulphoxide-D6. All the experiments were carried

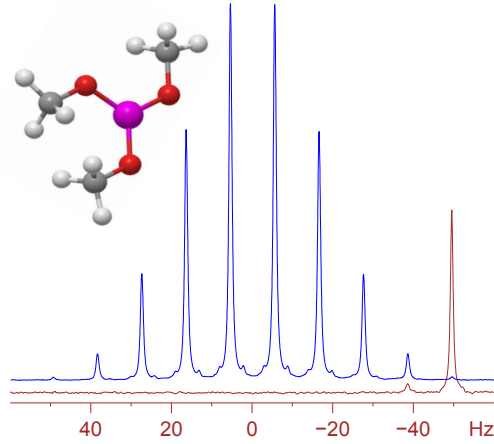


Fig. 3. The  $^{31}\text{P}$  spectra corresponding to single quantum excitation from thermal equilibrium (upper trace) and after converting the NOON state into the single quantum coherence using a CNOT gate (lower trace). The inset displays the molecular structure of trimethylphosphite ( $\text{P}(\text{OCH}_3)_3$ ).

out on a 500 MHz Bruker NMR spectrometer at an ambient temperature of 300 K. Each of the nine magnetically equivalent  $^1\text{H}$  spins are coupled to the  $^{31}\text{P}$  spin via indirect spin-spin interaction with a coupling constant of  $J = 11$  Hz thus forming an  $\text{AM}_9$  spin system. Accordingly phosphorous spectrum splits into 10 lines as shown in Fig. 3. An initial INEPT transfer was used to enhance the  $^{31}\text{P}$  polarization. Then, as described in the previous section, NOON state was prepared with a pseudo-Hadamard gate and a subsequent CNOT gate, and is converted back to a single quantum coherence using a second CNOT. The selection PFGs were adjusted such that  $G_3/G_2 = 9\gamma_H/\gamma_P + 1 = 23.23$ , to select the 10-quantum coherence pathway. A two-step phase cycle of  $\tilde{X}_M$  pulse of the first CNOT along with the receiver phase helped to reduce artifact signals. The single transition in  $^{31}\text{P}$  spectrum of Fig. 3 indicates the selection of NOON-state coherence pathway.

We first carried out the single quantum diffusion experiment as described in Fig. 1. The parameters of the experiment are shown in Fig. 4a. While keeping all other parameters fixed, we varied only the strength of the PFGs  $G_1$  in the range 0 to 0.3325 T/m in 20 equal intervals. The integrated intensity of the  $^1\text{H}$  signal as a function of  $G_1$  is shown in Fig. 4a. The diffusion constant,  $D = (6.24 \pm 0.06)10^{-10} \text{ m}^2 \text{ s}^{-1}$  was obtained by fitting these data points to the Gaussian expression given in (6).

Then we prepared the NOON state as explained above, and diffusion experiment was carried out as in Fig. 2. The main parameters of the experiment are shown in Fig. 4b. The lopsidedness for this system is  $l = 9.4$  and accordingly the NOON state experiment requires much shorter  $\Delta$  and  $\delta$  values to reach similar attenuation of the echo signal as that of the single quantum experiment. In Fig. 4b, the integrated intensity of the single transition, after

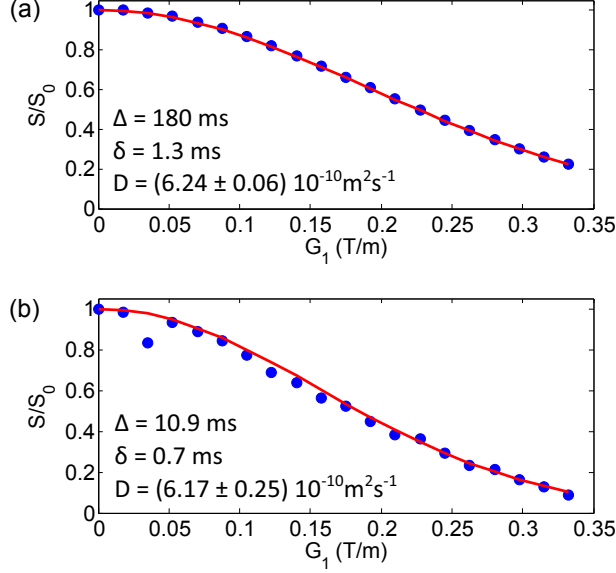


Fig. 4. Intensity of the echo signals as a function of the gradient strength  $G_1$  with (a)  $^1\text{H}$  single quantum coherence and (b) NOON state. The dots represent the experimental data and the lines represent the Gaussian fit. The insets in both the figures display the parameters of the experiments.

the selection of NOON-state coherence pathway, is plotted against  $G_1$ . The Gaussian fit, again using the expression (6), with  $\gamma_{\text{eff}} = l\gamma_H$  lead to the diffusion constant  $D = (6.17 \pm 0.25)10^{-10} \text{ m}^2 \text{ s}^{-1}$ . While the two methods gave identical values for the diffusion constant, the error-bar is slightly larger in the latter case due to the added complexity of the circuit, the imperfections in the selection of coherence pathway, reduced signal to noise, and due to the faster relaxation of the NOON state. On the otherhand, the shorter timescales of the NOON-state experiment suggests its possible applications in studying slow diffusion or studying diffusion with limited PFG strengths.

## 4 Conclusions

We described the application of NOON states in studying translational diffusion in liquids. Although the basic principle is general, the method is particularly convenient in the presence of a set of magnetically equivalent nuclei interacting with a heteronucleus via J-coupling. We have demonstrated the experimental measurement of diffusion constant in trimethylphosphite, which is a  $AM_9$  spin system. Both single-quantum and the NOON-state experiments lead to identical values for the diffusion constant, but the error-bar was slightly larger in the latter case due to the additional complexities. However, the NOON state experiment required weaker pair of PFGs and an order of magnitude shorter duration between them, indicating the possible applications in studying slow diffusion. The other available method for measurement

of slow diffusion involves the use of long-lived singlet states [17], which requires a pair of weakly interacting homonuclear spins spatially isolated from the rest of the spins [30]. In the current method we prepare a state that is highly sensitive to the gradient encoding of the z-coordinate and hence is able to capture the effects of diffusion even in shorter time-scales and with weaker PFGs. It might also be possible to combine the NOON state technique with the single scan techniques to achieve ultra-fast diffusion measurements. Such an experiment will then allow studying dynamic situations with time-varying diffusion constants.

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